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Heavy metals in Neogene sedimentary rocks as a potential geogenic hazard for sediment, soil, and surface and groundwater contamination (eastern Posavina and the Lopare Basin, Bosnia and Herzegovina)

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Abstract: The influence of geochemical processes (weathering, erosion and dilution) of the Internal Dinarides to the Posavina Neogene Basin and their implication to the pollution of the Sava River sediments at four sampling sites in the Eastern Posavina (Županja, Brčko, Bosanska Rača and Sremska Mitrovica) was studied. For this purpose, comparison of contents of heavy metals (Pb, Zn, Cu, Ni, Cr, Cd, As and Hg) of the Eastern Posavina sediments with local background values was performed. Sediments from two boreholes of the Lopare Basin considered as non-polluted and representative for specific geologic and hydrogeologic system were used for the calculation of local background values. The aim was to assess whether the observed heavy metals concentrations at four sampling sites along the Sava River represent background/natural or anthropogenic contamination. This task was performed using the geo-accumulation index and total enrichment factor. According to values of the total enrichment factor (0.25–0.71), the anthropogenic impact on the investigated area was quite low. The heavy metals contents in river sediments, soil and groundwater were mainly controlled by geochemical processes, particularly weathering (chemical proxy of alteration value ≈ 60). The results also offer novel insights into the elevated geogenic levels of Cr and Ni in the Eastern Posavina region.

Keywords: pollution; river sediments; geo-accumulation index; total enrichment factor; weathering.

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INTRODUCTION

The assessment of heavy metal pollution in fluvial sediments is a complex process, in which physical, chemical and biological data are required. Since in many areas the necessary biological data are not available, in environmental geochemistry, the assessment of the contamination status is normally based on Sediment Quality Guidelines (SQGs) or quantitative indexes such as the enrichment factor with respect to reference values, such as regional/local background values or average concentrations of shale, average continental crust or upper continental crust, *etc.*¹

The key environmental problem in the Sava River Basin is often directed to the release of contaminated untreated effluents from municipalities and industrial facilities. However, recent investigations showed that the sedimentary rocks from the Lopare Basin contain relatively high heavy metal concentrations.² Since, erosion activity weather these rocks to soils, the high heavy metal contents represent a significant geogenic hazard and could potentially represent a hazard for surface and groundwater, as well.² It is known that the majority of the clastic material was transported to the Eastern Posavina region by rivers and streams from the Bosnian Mountains.³ This was confirmed by the mineral composition of fluvial sediments, which originated from the serpentinite zone in Bosnia.³ The main direction of transport from south to north correlates with reducing proportions of coarse-grained clasts and a decreasing grain size in the same direction.⁴ In this way, in the southern part, along the Sava River, gravels are predominantly deposited, and sands in the northern sections.⁵

The catchments of Drina and Bosna Rivers are much larger than the catchments of rivers from the Papuk Mountains in the north of the Posavina Basin (Fig. S-1 of the Supplementary material to this paper). Consequently, sediments from the south should dominate sediments in this part of the Sava River, respectively the Posavina region. In this paper, the influence of geochemical processes of sediments from the Lopare Basin, which is drained by the Drina and Bosna Rivers, on the eastern part of the Neogene Posavina Basin (Eastern Posavina region) was studied. The contents of eight heavy metals (Pb, Zn, Cu, Ni, Cr, Cd, As and Hg) of the Eastern Posavina region (Županja, Brčko, Bosanska Rača and Sremska Mitrovica) were taken from published data.⁶ For local background values, the average concentration of the eight heavy metals (Zn, Cu, Cd, Pb, Cr, Ni, As and Hg) from two sediment boreholes, POT 1 (depth from 18.5 to 193 m) and POT 3 (depth from 27.8 to 344 m), of the Neogene Lopare Basin (Fig. S-1; Table S-I of the Supplementary material) were used. These sediments are considered as non-polluted and representative for this specific and unique geologic and hydrogeologic system.

In the investigated Neogene basins, a significant influence of regional and local hydrogeological relations as part of the system of groundwater circulation

was observed. The most important aquifers within the alluvial formations are in the terrains of northern Bosnia. Given the thickness of the gravel–sand formations and spatial position in relation to rivers, the conclusion may be drawn that the presence of aquifers is almost regularly found in direct hydraulic contact with renewable quantities of groundwater. The water quality is directly dependent on the lithologic composition of the hinterland.⁹ According to the aquifer characteristics, the first and partly the second hydrogeological groups are present in the investigated region. Group I (in the northern region) represents a high water-rich aquifer with a high transmissibility coefficient (more than $10^{-3} \text{ m}^2 \text{ s}^{-1}$). Group II, in the southern part (the region of Majevisa; Fig. S-1) is a medium water-rich aquifer and it is characterized by an intermediate transmissibility coefficient ($10^{-3} \text{ m}^2 \text{ s}^{-1}$). This is a very important factor in regard to processes such as dilution by tributaries and hill slope erosion from the Bosnian Mountains in the upper part of sediments of the tributaries of the Sava River, namely from the Majevisa Mountains, and the Bosna and Drina Rivers in the eastern Posavina region. Therefore, the aspect of weathering processes to soils as a potential hazard for surface and groundwater contamination in this region was also investigated.

MATERIALS AND METHODS

The investigated region included the eastern part of the Posavina Basin (sampling sites Županja, Brčko, Bosanska Rača and Sremska Mitrovica), the Lopare Basin and the Drina and Bosna River catchment (Fig. S-1). This unique region represents a part of the Internal Dinarides, which are formed between the Dinaric Ophiolite belt and the Sava–Vardar Zone. From geologic and hydro-geologic points of view, it belongs to the unique Sava–Vardar nappe and terrain with aquifers of intergranular porosity.⁹ It was formed during a late stage of orogeny in the Dinarides by extensional tectonic processes and it is considered to be a part of the wider Pannonian Basin and trapped sediments from the surrounding Alpine–Carpathian–Dinarian source area.

The Lopare Basin is a depression between the main Majevisa ridge to the south, which divides the Lopare and Tuzla Basins, and the northern Majevisa ridge, which is a natural border to the Posavina Basin (Fig. S-1).

The investigated sampling sites (along the Sava River), Brčko and Bosanska Rača are situated in the northeastern (NE) part of Bosnia and Herzegovina; Županja is located in the NE part of Croatia; and Sremska Mitrovica, is located in the northwestern part of Serbia (Fig. S-1).

From a total of 46 sediment samples from two boreholes POT-1 (depth to 193 m) and POT-3 (depth to 344 m) (Table S-I), a quarter of the core for analysis was taken using the “dot method”. Firstly, the sediment samples were dried at 105 °C. In the next step, the samples were successively ground in three stages to a grain size less than 2.36 mm. The samples were first grinded by a jaw crusher, than by cone crusher and finally by a roller crusher. After this stage, the samples were homogenized. The rough mill fragmented samples were subsequently finely pulverized and sieved into a grain size fraction < 63 µm.

The contents of heavy metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The ICP-AES measurements were performed using a Thermo Scientific iCAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, UK) spectrometer equipped with RACID86 Charge Injector Device (CID) detector, pneumatic cross-flow

type nebulizer, quartz torch, and alumina injector, which enabled the detection of samples containing HF in a small amount. Nitric acid (HNO₃, 65 %), hydrochloric acid (HCl, 37 %), orthophosphoric acid (H₃PO₄, 85 %) and hydrofluoric acid (HF, 50 %) were used for digestion. The experimental procedure was explained in detail in a previous paper.¹⁰

RESULTS AND DISCUSSION

Heavy metal content in background sediments

The background levels of heavy metals were uniformly distributed with depth of the sediment within the boreholes POT 1 and POT 3 (Table S-I). The content of almost all heavy metals were generally high compared to standard values (Tables S-I and I). According to their lithologically homogeneous composition and the uniform distribution of metals (Table S-I), it can be concluded that they were derived predominantly from homogeneous natural sediment sources and could, therefore, be used as background levels for surface sediments of the Sava River in the eastern Posavina Basin to determine the difference between the geogenic and anthropogenic sources. For background levels of heavy metals in the Lopare Basin sediments, the average reduced value in relation to the amount of diluted calcium carbonate¹¹ of the two boreholes POT 1 and POT 3 (Table I) was used. The amount of diluted calcium carbonate was calculated from the CaO contents in the sediments.^{2,10} The shallowest sample from borehole POT 1, which had a sandy clay composition as the result of weathering, (sample at a depth of 11.85 m; Table S-I) was excluded from the calculation of the background levels.

TABLE I. Values of the total element concentrations (mg kg⁻¹) in sediments of the Sava River (up to 15 cm),⁶ values of the local background and reference standards

Sampling site	Pb	Zn	Cu	Ni	Cr	Cd	As	Hg
Županja	33.9	134.0	31.1	212.0	381.0	0.47	19.8	0.27
Brčko	52.0	165.0	43.4	185.0	312.0	0.62	16.7	0.30
Bosanska Rača	122.0	184.0	47.1	186.0	273.0	0.66	17.9	0.37
Sremska Mitrovica	79.0	275.0	44.9	177.0	276.0	0.84	23.6	0.44
Local background values ^a	136.8	49.4	26.2	135.8	159.4	1.02	20.6	0.53
ISQG ^b	30.2	124.0	18.7	–	52.3	0.70	7.2	0.17
ÖNORM S 2088-2 ^c	100.0	300.0	100.0	60.0	100.0	1.00	20.0	1.00
FBiH 72/09 ^d	125.0	250.0	100.0	62.5	125	1.88	25.0	1.88
PEL ^e	112.0	271.0	108.0	–	160.0	4.20	41.6	0.49

^aThe average reduced value in relation to the amount of diluted calcium carbonate of two boreholes POT 1 and POT 3.¹¹ The shallowest sample from POT 1 with a sandy clay composition was excluded because of weathering processes; ^binterim sediment quality guideline (ISQG) values correspond to the threshold level effects below which diverse biological effects are not expected (Canadian Sediment Quality Guidelines for the Protection of Aquatic Life);¹² ^cAustrian Standards on Contaminated Land Management general protocol and generic criteria (trigger values) for risk assessment regarding human exposure and plant uptake (ÖNORM S 2088-2) for soil samples from 0 to 20 cm in depth;¹³ ^dguideline for the determination of permitted quantities of harmful and hazardous substances in soil and methods of their investigation (published in an Official Gazette of the Federation of Bosnia and Herzegovina, No. 72/09);¹⁴ ^eprobable effect level (PEL) characterizes the concentrations of pollutants that may affect aquatic life (Canadian Sediment Quality Guidelines for the Protection of Aquatic Life)^{12,15}

Distribution of heavy metals in the eastern Posavina region

Most of concentrations in the sediments at the sampling sites exceeded the Interim Sediment Quality Guideline (ISQG)¹² values, but they were notably lower in comparison to the Austrian Standard, ÖNORM S 2088-2,¹³ and the Bosnian and Herzegovinian Guideline for the determination of the permitted quantities of harmful and hazardous substances in the soil and the methods of their investigation, FBiH 72/09¹⁴ values (Table I). The contamination gradation increased from Županja to Sremska Mitrovica, with the exception of Ni and Cr. At all sampling locations, the concentrations of Cr were higher than the probable effect level, PEL^{12,15} (160.0 mg kg⁻¹ of Cr), ISQG¹² (52.3 mg kg⁻¹ of Cr), ÖNORM S 2088-2¹³ (100.0 mg kg⁻¹ of Cr) and FBiH 72/09¹⁴ (125.0 mg kg⁻¹ of Cr) values. However, interestingly, the local background values of 159.4 mg kg⁻¹ for Cr were also much higher than ISQG,¹² but very similar to PEL^{12,15} and closer to the ÖNORM S 2088-2¹³ and FBiH 72/09¹⁴ values (Table I). A similar observation found for the Ni and Pb contents. The contents of Cr and Ni were much higher than those for average continental mudstones.¹⁶ It is also evident, that compared to the standards ÖNORM S 2088-2¹³ and FBiH 72/09,¹⁴ the most representative comparative results were obtained in this study, because their values were the most similar ones to the element concentrations in the Sava River sediments and the local background values. Elevated Ni and Cr contents may result from ophiolites (ocean floor on land that is usually rich in some heavy metals, such as Cr and Ni) occurring in the neighborhood (Dinaric Ophiolite Belt).¹⁷ Alluvial flooding by the Bosna River, which drains the Central Dinaric Ophiolite Belt (CDOB) of Central Bosnia, resulted in abnormally high concentration of Cr (502 mg kg⁻¹) in the easternmost part of the Posavina area. The highest content of Cr in the sample of the site Županja (381.0 mg kg⁻¹ of Cr; Table I) also corroborates this hypothesis. In the absence of industrial pollutants in the wider area, all the elevated concentrations of Cr in the Pannonian region are assumed to be of geogenic origin.¹⁸

The Bosanska Rača and Sremska Mitrovica samples had on average higher concentrations of heavy metals than the samples from Županja and Brčko (Table I), consistent with the quantity of material that flows close to these sites from the Drina River, which is a confluent of the Sava River. During geological time, the Drina River changed its flow into the Mačva lowlands from east to west and formed the spacious terrace plane. The Sava River flow has a direct influence in the draining and inundation of the alluvial plane and the fuelling of minor flows and ground-water aquifers below the average river level during maximum water level events.¹⁹

Calculation of background/natural and anthropogenic contaminated levels

The use of the total concentrations as a criterion to assess the potential effects of a sediment concentration implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable.²⁰ In this study, the geo-accumulation index (I_{geo}) and the total enrichment factor (R) were used as tools for understanding the geogenic *versus* anthropogenic hazards.

The geo-accumulation index (I_{geo}) was originally defined by Müller (1979)⁷ for metal concentrations in pulverized sediment fractions (<2 µm). A previous expression on sediment fractions (less than 63–65 µm) combined with regional backgrounds was also established.²¹ The same approach was performed in this study.

The I_{geo} was developed for global standard scale values, which is expressed as follows:

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (1)$$

where C_n is the measured concentration of metal n in the sediment, which was taken from a published study,⁶ B_n is the geochemical background value for the metal n (heavy metal concentration in background sediment, Table I), and the factor 1.5 is incorporated in the relationship to account for possible variation in the background data due to lithologic effects.

The geo-accumulation index (I_{geo}) scale consists of seven grades (0 to 6) ranging from unpolluted to very strongly polluted (Table II).⁷ The I_{geo} values of the investigated sediments are given in Table III.

TABLE II. The geo-accumulation index (I_{geo}) scale (after Müller, 1979)⁷

I_{geo}	Class	Pollution intensity
>5	6	Very strongly polluted
4–5	5	Strongly to very strongly polluted
3–4	4	Strongly polluted
2–3	3	Moderately to strongly polluted
1–2	2	Moderately polluted
0–1	1	Unpolluted to moderately polluted
0	0	Unpolluted

The analytical data corresponding to each sampling site can be used for the calculation of an enrichment factor (r), defined as the ratio:⁸

$$r = \frac{(C_{\text{sed}} - C_{\text{back}})}{C_{\text{back}}} \quad (2)$$

where C_{sed} is the content of a metal in each sample site (the value was taken from a published study⁶), while C_{back} is the mean concentration of the same metal for all the background sediment levels (Table I). The r values for the Sava River sediments sampling sites are given in Table III. The metals with $r > 1.0$ could be considered as indicators of anthropogenic metal pollution and used for evaluating the degree of pollution of the surface sediments by calculation of a total enrichment factor (R), for each site, by averaging the r values of all (n) indicator-metals as follow:

$$R = \frac{\sum r}{n} \quad (3)$$

R values exceeding 1.5 indicate high pollution. R values between 1.5 and 1 imply moderately pollution, whereas samples with R values below unity are considered as unpolluted or exposed to low pollution.⁸ As a synthetic multi-parameter indicator, R can be assumed as an integrated index of the local metal pollution pattern for sample sites: Županja, Brčko, Bosanska Rača and Sremska Mitrovica (Table III).

TABLE III. Values of the geo-accumulation index (I_{geo}), enrichment factor (r) and total enrichment factor (R) for the sampling sites of the Sava River sediments

Sampling site	Pb	Zn	Cu	Ni	Cr	Cd	As	Hg
I_{geo}								
Županja	-2.60	0.86	-0.34	0.06	0.67	-1.70	-0.64	-1.56
Brčko	-1.98	1.16	0.14	-0.14	0.38	-1.30	-0.89	-1.41
Bosanska Rača	-0.75	1.31	0.26	-0.13	0.19	-1.21	-0.79	-1.11
Sremska Mitrovica	-1.38	1.89	0.19	-0.20	0.21	-0.87	-0.39	-0.86
Mean values	-1.68	1.30	0.07	-0.10	0.36	-1.27	-0.68	-1.23
r								
Županja	-0.75	1.71	0.19	0.56	1.39	-0.54	-0.04	-0.49
Brčko	-0.62	2.34	0.66	0.36	0.96	-0.39	-0.19	-0.44
Bosanska Rača	-0.11	2.73	0.80	0.37	0.71	-0.35	-0.13	-0.30
Sremska Mitrovica	-0.42	4.57	0.71	0.30	0.73	-0.18	0.14	-0.17
Mean values	-0.48	2.84	0.59	0.40	0.95	-0.37	-0.05	-0.35
R								
Županja					0.25			
Brčko					0.33			
Bosanska Rača					0.46			
Sremska Mitrovica					0.71			

In general, according to the R values below unity, the target area could be considered as exposed to low pollution. However, taking $r = 1.0$ as an operational threshold value, Zn at all sites and Cr at Županja could be considered as synthetic indicators of a local pattern of anthropogenic metal pollution, and furthermore, could be used for evaluating the degree of pollution of surface sediments. Based

on the mean value of r , the sediments are enriched in metals in the following order: $\text{Zn} > \text{Cr} > \text{Cu} > \text{Ni} > \text{As} > \text{Hg} > \text{Cd} > \text{Pb}$. In contrast to Zn and Cr, the other elements have values below unity. Elevated values for Zn and Cr most likely resulted from anthropogenic activities, considering that these metals have content at least two times higher than the background sediment (Table I). Moreover, the obtained results clearly show that Ni is not related to an anthropogenic source of pollution in any of the investigated sediments of the Sava River (Table III).

A gradient increase of the mean I_{geo} value in the following order: $\text{Zn} > \text{Cr} > \text{Cu} > \text{Ni} > \text{As} > \text{Hg} > \text{Cd} > \text{Pb}$ was observed. The I_{geo} index for Zn implies unpolluted to moderately polluted classification of the Županja site and moderately pollution for the other sites. The increase in this parameter for Zn values follows the course of the Sava River and because of the influence of its tributary Drina River, reaches the highest level of 1.89 in the Sremska Mitrovica sediments (Table III). In the group of the unpolluted to moderately polluted sites, the I_{geo} for Cr varies from 0.19 to 0.67, but in the opposite direction to the gradient of the Zn values. Higher values of r and I_{geo} indexes for Zn and Cr could be explained as being the result of geochemical processes, which will be discussed in the following paragraph.

Geochemical association significant for carbonate rock weathering and river transport

Weathering and erosion processes express themselves in the chemical composition of the so-called “Critical Zone” extending from the unweathered bedrock through soils to the atmosphere.²²

The chemical proxy of alteration, $\text{CPA} = [\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{Na}_2\text{O})] \times 100$ ²³ is a geochemical proxy for measuring the weathering intensity. It does not involve silicate CaO that is difficult to estimate in calcareous sediments or potassium because of its inconsistent behavior during chemical weathering. The index was proposed as a geochemical proxy of silicate weathering for loess and paleo-soils. As a proxy of the intensity of silicate weathering for the upper part of borehole POT 1 (sample 1 at a depth of 11.85 m; Table S-I, with values of 18.8 % for Al_2O_3 and 7.7 % for Na_2O), the CPA has a value of 60, indicating a relatively high intensity of alteration.²³

On larger spatial scales, rivers are natural integrators of these weathering and erosion products and fluxes over their drainage areas.²⁴ The hydrological differentiation processes that operate on river sediments combined with source rock composition and chemical weathering tend to produce sediment suites with different chemical compositions.^{25,26} As discussed above, the elevated Cr values are of geogenic origin and also the consequence of anomalies registered in the easternmost part of the Posavina area due to alluvial flooding by the Bosna River, which drains the Central Dinaric Ophiolite Belt. In the area of an active con-

tinental margin, an indented relief with several rises and troughs existed facilitating the emplacement of the olistostromes and the deposition of first overstep sequences, in which ophiolitic material was re-deposited. Sedimentation occurred in some areas in shallow-water environments and some of the rises emerged and the ophiolites underwent weathering according to models of the geodynamic evolution of the Central Dinarides.²⁷ This is likely one of several reasons for the elevated metal contents in the Posavina region. Considering the total enrichment factor (R), which is very low, there was no anthropogenic pollution following the Sava River flow from Županja to Sremska Mitrovica. When discussing river transport of heavy metals, it is interesting to mention that more than 97 percent of the mass transport of heavy metals to the oceans is associated with river sediments.²⁸ It is most likely that the geological weathering and river transport (Bosna and Drina Rivers) are the factors responsible for the increase in the concentration of the given heavy metals.

Zn represents a chemical element that was introduced mainly into the environment by the natural weathering of ore deposits. In the Pannonian region, the transport of fine fractions still occurs and results in the concentration of this group of elements being higher in the topsoil. In addition, the topographic depressions occurring in these evaporite karst areas are frequently prone to flooding either by the concentration of surface runoff or by groundwater flooding when the water table rises above the ground level,²⁹ thereby intensifying the process of diluting the sediment.

By reviewing the data from the flood hydrograph, it could be asserted that intensive floods occurred over a limited space. The most flood-prone area is the region called Donje Posavlje, downstream of Županja. The flood duration depends on the flood volume (measured by a hydrograph) and the size of the catchment. The flood duration of the Sava River near the Sremska Mitrovica sampling site is 40 to 70 days.³⁰

In historically or periodically flooded areas of the Pannonian region, the average concentrations of Cd (1.7 mg kg⁻¹ topsoil, 1.2 mg kg⁻¹ subsoil), Pb (170 mg kg⁻¹ topsoil; 130 mg kg⁻¹ subsoil) and Zn (470 mg kg⁻¹ topsoil, 390 mg kg⁻¹ subsoil)³¹ are similar to those observed in this study (Table II).

CONCLUSIONS

This study proves that the local background values of heavy metals in the sedimentary rocks play an important role in the interpretation of the level of geochemical hazard of the investigated region.

The geo-accumulation indexes (I_{geo})⁷ and the total enrichment factors (R)⁸ were calculated to assess whether the observed concentrations represent background/natural or anthropogenic contamination.

Analyzing the significance of I_{geo} , R and chemical proxy of alteration (CPA) leads to the conclusion that weathering, erosion and dilution during aquatic transport are the major factors regarding their effects on the various environmental media (sediments, soil, surface and groundwater). The aspect of the weathering process to soils is a potential hazard for surface and groundwater in the Eastern Posavina region. Based on the geologic processes associated with sediment transfer from source to sink, geochemical principles play a major role in defining the origin of the heavy metal pollution levels in the region.

A geogenic hazard is generated by primary enrichment in rocks, processes of weathering and hill slope erosion as factors that determine the source of pollution in the investigated region. In this paper, based on European (Austrian) ÖNORM S 2088-2 and Bosnian and Herzegovinian FBiH 72/09 values, it was clearly shown that the high local geogenic background values exclude a dominant anthropogenic influence on the high heavy metal contents (*e.g.*, Cr and Ni) in the river sediments.

SUPPLEMENTARY MATERIAL

Figure S-1 and Table S-I are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

САДРЖАЈ ТЕШКИХ МЕТАЛА У НЕОГЕНИМ СЕДИМЕНТНИМ СТЕНАМА – МОГУЋИ РИЗИК ОД НАТИВНОГ ЗАГАЂЕЊА СЕДИМЕНАТА, ЗЕМЉИШТА, ПОВРШИНСКИХ И ПОДЗЕМНИХ ВОДА (ИСТОЧНА ПОСАВИНА И ЛОПАРСКИ БАСЕН, СЕВЕРОИСТОЧНА БОСНА И ХЕРЦЕГОВИНА)

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Испитиван је утицај геохемијских процеса (атмосферског деловања на стене, ерозије и разблаживања) унутрашњих Динарида на Посавски неогени басен и њихове импликације на загађивање седимената реке Саве са 4 локације у источној Посавини (Жупања, Брчко, Босанска Рача и Сремска Митровица). У том циљу изведено је поређење садржаја тешких метала (Pb, Zn, Cu, Ni, Cr, Cd, As и Hg) у седиментима са наведених локација са просечним локалним садржајима ових елемената у нативним незагађеним седиментима. Просечни локални садржај тешких метала израчунат је на основу њиховог садржаја у незагађеним седиментима из две бушотине лопарског басена који је репре-

зентативан за овај специфичан геолошко-хидрогеолошки систем. Циљ рада је био да се процени да ли је повећан садржај тешких метала на 4 локалитета дуж реке Саве последица природног или антропогеног загађења. У ту сврху примењени су индекс геоакумулације и укупни фактор обогаћења. На основу вредности укупног фактора обогаћења (0,25–0,71) утврђено је да је утицај антропогеног загађења у испитиваном региону веома низак. Садржај тешких метала у седиментима, земљишту и подземним водама претежно је контролисан геохемијским процесима, посебно атмосферским деловањем на стене (хемијски индекс промене ~60). Резултати овог испитивања такође су омогућили нови начин сагледавања нативно повишених концентрација Cr и Ni у региону источне Посавине.

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REFERENCES

1. H. Ho, R. Swennen, A. Van Damme, *Geol. Belg.* **13** (2010) 37
2. N. Grba, F. Neubauer, A. Šajnović, B. Jovančičević, in *Geophysical Research Abstracts of the European Geosciences Union – General Assembly*, Vienna, Austria, 2014, [EGU2014-10850] (in press)
3. R. Mutić, *Acta Geol.* **23** (1993) 1
4. K. Urumović, Z. Hernitz, J. Šimon, *Geol. Vjesnik* **30** (1978) 297 (in Serbo-Croatian)
5. P. Miletić, A. Bačani, D. Mayer, A. Capar, *Geol. Vjesnik* **39** (1986) 137 (in Serbo-Croatian)
6. R. Milačić, J. Ščančar, S. Murko, D. Kocman, M. Horvat, *Environ. Monit. Assess.* **163** (2010) 263
7. G. Müller, *Umschan* **79** (1979) 778
8. G. Adami, P. Barbieri, E. Reisenhofer, *Toxicol. Environ. Chem.* **77** (2000) 189
9. http://aoa.ew.eea.europa.eu/tools/virtual_library/bibliography-details-each-assessment/answer_0519986588/w_assessment-upload/index_html?as_attachment:int=1 (last accessed April 26, 2014)
10. N. Grba, A. Šajnović, K. Stojanović, V. Simić, B. Jovančičević, G. Roglić, V. Erić, *Chem. Erde-Geochem.* **74** (2014) 107
11. R. Wehausen, H.-J. Brumsack, in *Proceedings of the Ocean Drilling Program, Scientific Results*, A. H. F. Robertson, K.-C. Emeis, C. Richter, A. Camerlenghi, Eds., Texas A&M University, College Station, TX, 1998, p. 207
12. https://www.elaw.org/system/files/sediment_summary_table.pdf (last accessed April 26, 2014)
13. ÖNORM S 2088-2: *Austrian Standards on Contaminated Land Management: Risk assessment for polluted soil concerning impacts on surface environments*, 2000
14. <http://www.uip-zzh.com/files/zakoni/poljoprivreda/72-09.pdf> (last accessed April 26, 2014)
15. Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec, *Criteria for the Assessment of Sediment Quality in Quebec and Application Frameworks: Prevention, Dredging and Remediation*, 2007, p. 7
16. M. Brown, T. Rushmer, *Evolution and Differentiation of the Continental Crust*, Cambridge University Press, New York, USA, 2008, p. 92
17. K. Ustaszewski, S. M. Schmid, B. Lugović, R. Schuster, U. Schaltegger, D. Bernoulli, L. Hottinger, A. Kounov, B. Fügenschuh, S. Schefer, *Lithos* **108** (2009) 106
18. J. Halamić, Z. Peh, S. Miko, L. Galović, A. Šorša, *J. Geochem. Explor.* **115** (2012) 36

19. M. Gajić, S. Vujadinović, *Glasnik srpskog geografskog društva* **89** (2009) 115 (in Serbian)
20. A. Tessier, P. G. C. Campbell, M. Bisson, *Anal. Chem.* **51** (1979) 844
21. B. Rubio, M. A. Nombela, F. Vilas, *Mar. Pollut. Bull.* **40** (2000) 968
22. S. L. Brantley, M. Lebedeva, *Annu. Rev. Earth Planet. Sci.* **39** (2011) 387
23. B. Buggle, B. Glaser, U. Hambach, N. Gerasimenko, S. Marković, *Quatern. Int.* **240** (2011) 12
24. B. A. McKee, R. C. Aller, M. A. Allison, T. S. Bianchi, G. C. Kineke, *Cont. Shelf Res.* **24** (2004) 899
25. H. W. Nesbitt, G. M. Young, *J. Geol.* **97** (1989) 129
26. P. W. Fralick, B. I. Kronberg, *Sediment. Geol.* **113** (1997) 111
27. J. Pamić, I. Gušić, V. Jelaska, *Tectonophysics* **297** (1998) 251
28. C. K. Jain, C. K. Sharma, *J. Hydrol.* **253** (2001) 81
29. F. Gutiérrez, A. H. Cooper, K. S. Johnson, *Environ. Geol.* **53** (2008) 1007
30. http://www.savacommission.org/dms/docs/dokumenti/srbmp_micro_web/backgroundpapers_final/no_9_background_paper_integration_of_water_protection_in_developments_in_the_sava_rb.pdf (last accessed April 26, 2014)
31. R. Šajn, J. Halamić, Z. Peh, L. Galović, J. Alijagić, *J. Geochem. Explor.* **110** (2011) 278.